

Upper and Lower Bounds to Atomic and Molecular Properties. I. Be-Sequence Oscillator Strengths (Dipole-Length Formulation) for the $1s^2 2s^2 {}^1S - 1s^2 2s 2p {}^1P$ Transition

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Wave functions, which include interelectron coordinates r_{ij} explicitly, are calculated for the $1s^2 2s^2 {}^1S$ and $1s^2 2s 2p {}^1P$ states of Be I, C III, and O V. These wave functions are used to calculate oscillator strengths, including upper and lower bounds, for the lowest ${}^1S - {}^1P$ transition. Interpolation techniques are used to make a graphical study of the oscillator-strength behavior along the isoelectronic sequence. Comparisons are made with previous experimental and theoretical results. The results of this study are oscillator strengths for the $1s^2 2s^2 {}^1S - 1s^2 2s 2p {}^1P$ Be isoelectronic sequence with rigorous upper and lower bounds of (7-10)% and probable accuracy $\leq 2\%$.

I. INTRODUCTION

Spectroscopic data for atoms and ions fall into a category of fundamental scientific material for which justification of measurement or calculation is scarcely necessary. The measurement of the wavelengths of spectral lines and the subsequent deduction of energy levels is usually not too difficult.^{1,2} The study of the strengths (intensities) of spectral lines is, however, a much more formidable problem.³ On the experimental side, absolute oscillator strengths, or f values, are typically determined with uncertainties of 10-20% or more.⁴ On the theoretical side, Pekeris and co-workers appear to have established some helium f values to 1% or better,⁵ and other transitions in the two-electron isoelectronic sequence have been determined to perhaps 5%.^{6,7} But results reliable to better than 10-20% have not been generally accessible in larger systems.^{8,9} In addition, the question of the reliability of theoretical predictions has become increasingly acute,¹⁰ and there is a need for procedures which lead to upper and lower bounds for the properties of interest, so that rigorous error limits are attached to the error estimates. In view of the above, we have calculated f values for the ${}^1S - {}^1P$ transition (by the dipole-length formulation) for some members of the beryllium isoelectronic sequence, and used the interpolation techniques (based on Rayleigh-Schrödinger perturbation theory) of Wiese and Weiss¹¹ to make a graphical study of the f -value behavior along the isoelectronic sequence. The calculations utilize the best wave functions (on any energy criterion) currently available.^{12,13} In addition, the procedure of Weinhold^{14,15} has been used to calculate upper and lower bounds to the computed f values. The results of this study are oscillator strengths for the $1s^2 2s^2 {}^1S - 1s^2 2s 2p {}^1P$ Be isoelectronic sequence

with rigorous upper and lower bounds of 7-10% and probable accuracy $\leq 2\%$.

II. THEORY

A. Wave Functions

La Paglia and Sinanoglu¹⁶ have shown that for the resonance transition of the beryllium isoelectronic sequence ($1s^2 2s^2 {}^1S - 1s^2 2s 2p {}^1P$), Hartree-Fock wave functions are unreliable and wave functions, including correlation effects, of considerable accuracy must be employed, not only for the ground state, but also for excited states. The procedure adapted here for incorporating correlations into the wave function is the method of Sims and Hagstrom,¹³ in which a variational trial function is written as a linear combination of known many-electron functions,

$$\Psi = \sum_k C_k \Phi_k, \quad (1)$$

and the configurations Φ_k are themselves antisymmetrized, projected products of orbitals and interelectronic coordinates. By minimizing the energy with respect to the coefficients C_k , one is led to the usual matrix eigenvalue equation for the energy and the coefficients C_k . The eigenvalues are always upper bounds to the energy of the corresponding excited (or ground) state.¹⁷ The eigenvalue equation is solved by Jacobi's method¹⁸ after the overlap matrix has been triangulated and the Hamiltonian matrix transformed by the method of Michels, Van Dine, and Elliott.¹⁹

In Eq. (1), the Φ_k are

$$\Phi_k = O(L^2) O_{as} \left(\chi_k r_{ij}^{v_k} \prod_{s=1}^4 \phi_{ks}(\vec{r}_s) \right), \quad (2)$$

where $O(L^2)$ is an idempotent orbital-angular-momentum projection operator²⁰ and O_{as} is the

projection operator that guarantees the antisymmetry of the wave function

$$O_{as} = (4!)^{-1} \sum_P (-1)^p P, \quad (3)$$

where the summation runs over all the $4!$ permutations P , with p being the parity of the corresponding permutation P . For this work, the spin function was taken as $\chi_k = \chi = \frac{1}{2}(\alpha_1\beta_2 - \beta_1\alpha_2) \times (\alpha_3\beta_4 - \beta_3\alpha_4)$, which has $S = S_z = 0$. In Eq. (2), $\phi_{ks}(\vec{r}_s)$ refers to the s th basis orbital in the k th configuration. The orbital basis consists of Slater-type orbitals (STO's) of the general form

$$\phi(\vec{r}) = \frac{(2\xi)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\xi r} Y_{l,m}, \quad (4)$$

where the set $\{Y_{l,m}\}$ consists of normalized spherical harmonics in the Dirac phase convention.²¹ In Eq. (2), the restriction of only one r_{ij} coordinate per term, first proposed by James and Coolidge,²² has been retained. The basis set consists of s and p Slater-type orbitals (STO's) and powers of interelectronic coordinates: r_{ij}^v ($v=0, 1, 2$). Previous calculations¹³ have shown that this is an excellent basis set for beryllium.

B. Oscillator Strengths

The basic theory of electric dipole radiation in atomic systems is given by Condon and Shortley,²¹ and we follow their terminology closely. Assuming Russell-Saunders (LS) coupling and the nonrelativistic many-electron Hamiltonian (Hartree atomic units)²³

$$H = \sum_{i=1}^N \left(\frac{1}{2} \Delta_i - \frac{Z}{r_i} \right) + \sum_{i<j} \frac{1}{r_{ij}}, \quad (5)$$

the energy states of an atom are characterized by the set of quantum numbers $\gamma LSM_L M_S$. Here γ denotes the electronic configuration, L the total angular momentum, S the total spin, and M_L and M_S are the projections of L and S , respectively, on the axis of quantization.²⁴ For an electric dipole transition connecting the terms (multiplets) γLS and $\gamma' L'S'$, Condon and Shortley introduced the quantity $\mathfrak{S}(\gamma LS; \gamma' L'S')$, called the absolute multiplet strength. It is defined in terms of the

electric-dipole-moment operator

$$\vec{P} = \sum_{i=1}^N \vec{r}_i$$

by²⁵

$$\mathfrak{S}(\gamma LS; \gamma' L'S') = \sum_{M_L, M_S} \sum_{M_L', M_S'} |\langle \gamma LSM_L M_S | \vec{P} | \gamma' L'S' M_L' M_S' \rangle|^2. \quad (6)$$

The f value or multiplet oscillator strength is related to \mathfrak{S} by

$$f(\gamma LS \rightarrow \gamma' L'S') = \frac{2}{3} \frac{E(\gamma' L'S') - E(\gamma LS)}{(2L+1)(2S+1)} \mathfrak{S}(\gamma LS; \gamma' L'S'). \quad (7)$$

The familiar electric dipole selection rules, $\Delta S=0$, $\Delta M_S=0$, $\Delta L=0, \pm 1$, and $\Delta M_L=0, \pm 1$, hold for the Hamiltonian we use. Moreover, given γLS and $\gamma', L' (=L-1, L, L+1) S' (=S)$, as a consequence of the Wigner-Eckart theorem,²⁶ every nonvanishing matrix element of the operator \vec{P} can be expressed in terms of a single parameter $\beta(\gamma LS; \gamma' L'S')$ multiplied by expressions involving only L, M_L , and M_L' . The parameter is independent of the quantum numbers M_L, M_L', M_S , and M_S' , the summation indices occurring in Eq. (6). Consequently, the expressions for the multiplet oscillator strength may be written as products of the parameter $\beta(\gamma LS; \gamma' L'S')$ and a single algebraic function of L and S resulting from the summation. Finally, notice that only one nonvanishing matrix element need be evaluated to determine $\beta(\gamma LS; \gamma' L'S')$, so that instead of computing all the matrix elements occurring in the summations occurring in Eq. (6), a single matrix element suffices to find the multiplet oscillator strength for given $\gamma LS, \gamma' L'S'$.

For the $1s^2 2s^2 {}^1S - 1s^2 2s 2p {}^1P$ transition, the 1S term consists of one state with $S=M_S=L=M_L=0$. The 1P term consists of three states corresponding to $S=M_S=0, L'=1$, and $M_L'=-1, 0, 1$. We choose to express $(\gamma LS \rightarrow \gamma' L'S')$ in terms of the matrix element corresponding to the 1P state with $S=M_S=0, L'=1$, and $M_L'=0$. Then Eq. (6) becomes (unnormalized wave functions), from Goldberg,²⁷

$$\mathfrak{S}(\gamma {}^1S; \gamma' {}^1P) = 3 \left| \frac{\int dx_1 \cdots dx_n \psi_\gamma^*({}^1S) \vec{P} \psi_{\gamma'}({}^1P, M_L'=0)}{[\langle \psi_\gamma({}^1S) | \psi_\gamma({}^1S) \rangle \langle \psi_{\gamma'}({}^1P, M_L'=0) | \psi_{\gamma'}({}^1P, M_L'=0) \rangle]^{1/2}} \right|^2, \quad (8)$$

and we need only construct $\psi_\gamma({}^1S)$ and $\psi_{\gamma'}({}^1P, M_L=0)$ and evaluate Eq. (8) to compute \mathfrak{S} .

It is generally known²⁸ that with $\psi_\gamma LSM_L M_S$ as exact eigenfunctions of H [Eq. (5)], the commuta-

tion relations of H with \vec{P} (dipole-length operator) lead to two additional relations for $\mathfrak{S}(\gamma LS; \gamma' L'S')$,⁸ which arise from the use of the dipole-velocity and dipole-acceleration operators given by

$$\vec{\nabla} = \sum_{i=1}^N \vec{\nabla}_i \quad (9)$$

and

$$\vec{A} = \sum_{i=1}^N \frac{Ze^2 \vec{r}_i}{|\vec{r}_i|^3}, \quad (10)$$

respectively. These three formulas are equivalent when one uses exact eigenfunctions of H [Eq. (5)] or of an independent-electron central-field-model Hamiltonian. However, they disagree whenever the eigenfunctions of a central-field model are improved by including some correlation, even by only the Hartree-Fock (HF) procedure.²⁹ Starace³⁰ has shown that the length formula is the physically correct one for all methods, such as Hartree-Fock, which involve the diagonalization of an approximate, but nonlocal, Hamiltonian. For the procedure we are using, which involves the use of a local potential, the use of the three different operators will give different results. It has been generally argued⁸ that, since the acceleration operator contains terms behaving as $1/r^2$, the dipole-acceleration form is most sensitive to the accuracy of the wave function in the immediate neighborhood of the nucleus, so that oscillator strengths computed with variationally stable approximate wave functions (emphasizing more distant regions) are not reliably given in terms of this operator. Since the dipole-length and dipole-velocity forms should agree as the wave function approaches the exact eigenfunction, some authors have taken the closeness of agreement of \mathcal{S} computed with dipole-length and dipole-velocity operators as a measure of the accuracy of their computation of \mathcal{S} , but there is now abundant evidence that this procedure is not very reliable.³¹ In the present work, we compute upper and lower bounds to the operator and use these theoretical bounds as a measure of the accuracy of the f value; we compute f values in terms of the dipole-length operator as given by Eq. (8).³²

To evaluate Eq. (8) we define

$$\begin{aligned} x_0(i) &= z_i = r_i \cos \theta_i = ar_i Y_{1,0}(i), \\ x_{+1}(i) &= -2^{-1/2}(x_i + i y_i) = ar_i Y_{1,1}(i), \\ x_{-1}(i) &= 2^{-1/2}(x_i - i y_i) = ar_i Y_{1,-1}(i), \end{aligned} \quad (11)$$

where $a = (\frac{1}{3} 4\pi)^{1/2}$ and the $Y_{l,m}$ are the same as in Eq. (4). Let

$$X_0 = \sum_{i=1}^N x_0(i), \quad X_{-1} = \sum_i x_{-1}(i), \quad X_1 = \sum_i x_1(i). \quad (12)$$

Then³³

$$|\vec{P}|^2 = |X_0|^2 + |X_{-1}|^2 + |X_1|^2. \quad (13)$$

Since $x_j(i) = \pm a [2, 1, j]_0^i$ in terms of unnormalized STO's defined by

$$[n, l, m]_S^i = r_i^{n-1} e^{-\zeta r_i} Y_{l,m}(i), \quad (14)$$

we obtain, for \mathcal{S} ,

$$\begin{aligned} \mathcal{S}(\gamma^1 S; \gamma^1 P) &= \left(\frac{4}{3}\pi\right) 3 \sum_{j=-1}^1 \left| \int dx_1 \cdots dx_n \psi_\gamma^*(1S) \right. \\ &\quad \left. \times \sum_{i=1}^N [2, 1, j]_0^i \psi_{\gamma'}(1P, M_{L'}=0) \right|^2 \end{aligned} \quad (15)$$

$$= 4\pi (|\vec{W}_{-1}|^2 + |\vec{W}_0|^2 + |\vec{W}_{+1}|^2)$$

$$= 4\pi |\vec{W}_0|^2, \quad (16)$$

owing to symmetry. (j must equal 0 or the integral vanishes.) In writing Eq. (15), we have assumed that ψ_γ and $\psi_{\gamma'}$ are normalized ($\langle \psi_\gamma | \psi_\gamma \rangle = 1$), and $|\vec{W}_j|$ is defined by

$$|\vec{W}_j| = \left| \int dx_1 \cdots dx_n \psi_\gamma^*(1S) \sum_{i=1}^N [2, 1, j]_0^i \psi_{\gamma'}(1P, M_{L'}=0) \right|. \quad (17)$$

To evaluate Eq. (16), we use the fact that the wave functions employed to evaluate Eq. (16) are given by Eq. (1) and are linear combinations of antisymmetrized, projected products of orbitals and interelectronic coordinates. Thus

$$|\vec{W}_j| = \sum_{K,L} C_K C_L |W_j|_{KL}, \quad (18)$$

where

$$|W_j|_{KL} = \langle \Phi_K | \sum_{i=1}^N [2, 1, j]_0^i | \Phi_L \rangle. \quad (19)$$

In Eq. (19), Φ_L is a linear combination of orbitals and interelectronic coordinates, so that Eq. (19) can be evaluated by expanding the product of $[2, 1, j]_0^i$ and the appropriate STO of Φ_L in terms of STO's by the formulas given in a previous paper.³⁴ Then the integrals required to evaluate Eq. (16) are similar in type to those required to calculate overlap matrix elements using these wave functions and can be evaluated as described later.

C. Upper and Lower Bounds to Oscillator Strengths

Weinhold¹⁴ has described a procedure for calculating rigorous upper and lower bounds to dipole strengths. If the exact transition moment is

$$W_{ab} = \langle \Psi_a | W_i | \Psi_b \rangle, \quad (20)$$

where Ψ_a and Ψ_b are the exact wave functions for states a and b , respectively, and W_i is some par-

ticular Cartesian component of the vector operator \vec{P} , then Weinhold's formula in terms of the estimate

$$\bar{W}_{ab} = \langle \psi_a | W_i | \psi_b \rangle, \quad (21)$$

where ψ_a and ψ_b are the approximate wave functions for states a and b , respectively, is

$$W_{ab} \leq S_{a\pm} S_{b\pm} \bar{W}_{ab} \pm \epsilon_{a+} S_{b\pm} \Delta_{ab} \pm \epsilon_{b+} \\ \times [\langle \Psi_a | W_i^2 | \Psi_a \rangle_+ - (S_{a-} \bar{W}_{ab} - \epsilon_{a+} \Delta_{ab})^2]^{1/2}. \quad (22)$$

Here $S_a \equiv \langle \psi_a | \Psi_a \rangle$, $S_b \equiv \langle \psi_b | \Psi_b \rangle$, i.e., the (positive) overlap integrals of the approximate wave functions ψ_a , ψ_b with the true wave functions Ψ_a , Ψ_b , and ϵ_{a+} , ϵ_{b+} are simply

$$\epsilon_{a+} \equiv (1 - S_{a-}^2)^{1/2}, \quad \epsilon_{b+} \equiv (1 - S_{b-}^2)^{1/2},$$

and Δ_{ab} is defined by

$$\Delta_{ab} \equiv (\langle \psi_b | W_i^2 | \psi_b \rangle - \bar{W}_{ab}^2)^{1/2}. \quad (23)$$

In Weinhold's scheme, \bar{W}_{ab} and $\langle \psi_b | W_i^2 | \psi_b \rangle$ are computed directly. Without loss of rigor, S_{a+} , S_{b+} may be taken to be 1, and for Ψ_a , Ψ_b , the lowest states of their respective symmetries, we can use the "Eckart criterion" to determine S_{a-} , S_{b-} ;

e.g.,

$$S_{a-}^2 = (E_a^* - \langle \psi_a | H | \psi_a \rangle) (E_a^* - E_a), \quad (24)$$

where E_a and E_a^* are the ground- and excited-state energy (with the same symmetry as the ground state) of the system with Hamiltonian H . The remaining unknown of relation (22) is the upper bound $\langle \Psi_a | W_i^2 | \Psi_a \rangle_+$. Weinhold presents several formulas for its treatment; we take

$$\langle \Psi_a | W_i^2 | \Psi_a \rangle \approx \langle \psi_a | W_i^2 | \psi \rangle, \quad (25)$$

where ψ is our highly accurate "S" wave function.

With $|W_j|$'s defined by Eq. (17), we have that

$$\mathcal{S}(\gamma^1 S; \gamma^1 P) = 4\pi |\bar{W}_0|^2 = 3 \bar{W}_{ab}^2, \quad (26)$$

so that

$$|\bar{W}_0| = (3/4\pi)^{1/2} \bar{W}_{ab}. \quad (27)$$

Relation (22) holds for $|\bar{W}_0|$ in place of W_{ab} if we compute $\langle \Psi_a | W_i^2 | \Psi_a \rangle$ by relation (25) and multiply by $3/4\pi$ to account for the difference between $|\bar{W}_0|$ and \bar{W}_{ab} given by Eq. (27). Also, the only remaining unknown in the calculation of upper and lower bounds to $|\bar{W}_0|$ is $\langle \psi_b | W_i^2 | \psi_b \rangle$.

With the aid of³⁴

$$[2, 1, j]_0^i [2, 1, j]_0^i = \sum_{P_a=0}^1 r_i^2 [(2l_1+1)/4\pi]^{1/2} C^1_1(1, j; 1, j) Y_{l_1, 0} \quad (l_1 = 2 - 2P_a) \\ = \sum_{P_a=0}^1 [(2l_1+1)/4\pi]^{1/2} C^1_1(1, j; 1, j) [3, l_1, 0]_0^i, \quad (28)$$

we obtain

$$\langle \psi_b | (3/4\pi) X_0 X_0 | \psi_b \rangle = \sum_{i=1}^4 \sum_{P_a=0}^1 [(2l_1+1)/4\pi]^{1/2} C^1_1(1, 0; 1, 0) \langle \psi_b | [3, l_1, 0]_0^i | \psi_b \rangle \\ + \sum_{\substack{i,k \\ i \neq k}} \langle \psi_b | [2, 1, 0]_0^i [2, 1, 0]_0^k | \psi_b \rangle. \quad (29)$$

Here $C^L(l^1, m^1; l, m)$ is the Condon-Shortley coefficient²¹ defined by

$$C^L(l^1, m^1; l, m) = [4\pi/(2L+1)]^{1/2} \int Y_L^{m^1-m}(\theta, \phi) Y_L^{m^1}(\theta, \phi) Y_L^m(\theta, \phi) \sin\theta d\theta d\phi.$$

The matrix elements in Eq. (29) are handled similarly to the way $|W_j|$ was treated earlier.

D. Trends of Oscillator Strengths Along the Be Isoelectronic Sequence

The use of interpolation techniques based on Rayleigh-Schrödinger perturbation theory to study systematic trends of f values along an isoelectronic sequence is due to Wiese and Weiss.¹¹ The fundamental idea is to scale all distances by the

nuclear charge Z and then apply conventional perturbation theory, treating the interelectronic repulsion as the perturbation:

$$H = \sum_i \left(\frac{-\Delta_i(\rho)}{2} - \frac{1}{\rho_i} \right) + \frac{1}{Z} \sum_{i < j} \frac{1}{\rho_{ij}} \\ = H_0 + \frac{1}{Z} V, \quad (30)$$

where $\rho = Zr$.

Perturbation theory then gives for the wave function and energy,

$$\Psi = \Psi_0 + (1/Z)\Psi_1 + \dots, \quad (31)$$

$$E = E_0 Z^2 + E_1 Z + E_2 + \dots. \quad (32)$$

Here Ψ_0 is just a configuration of hydrogenic orbitals, E_0 is the sum over all electrons of hydrogenic energies, and the first-order energy is given by

$$E_1 = \langle \Psi_0 | V | \Psi_0 \rangle. \quad (33)$$

If there is a degeneracy in zeroth order (as in the transition we are studying) then the first-order energy is found by diagonalizing the first-order energy matrix which removes the degeneracy and redefines the zeroth-order wave function as a linear combination of the degenerate hydrogenic configurations. This charge-expansion approach of Wiese and Weiss has also been used to calculate f values.³⁵ Dalgarno and co-workers,^{36, 37} working within this framework, have derived formulas for the multiplet strength as a function of Z by solving for the orbitals through first order and including the zeroth-order configuration mixing. The results of this method should be accurate for sufficiently large Z , and are presented in Fig. 1 (Z -expansion results) in extending the curves to $Z^{-1} = 0$. The multiplet strength, from Eqs. (6) and (31), has the Z dependence

$$S = S_0/Z^2 + S_1/Z^3 + \dots, \quad (34)$$

where S_0 is the multiplet strength obtained from hydrogenic functions and may well involve the first-order mixing. For the oscillator strength we are interested in, there is no change in principal quantum number so that the zeroth-order energy difference vanishes and the Z dependence of the f value is

$$f = f_1/Z + f_2/Z^2 + \dots, \quad (35)$$

so that the oscillator strength tends to zero for large Z .³⁸

These considerations have several consequences. In the first place, notice that Z^{-1} is the natural parameter against which to plot f values in a graphical display of the isoelectronic sequence. The entire sequence is then compressed in the region between $Z^{-1} = 0$ and the value of the neutral atom. Second, one can calculate relatively easily the way in which these curves start at the zero end, in this case, from the slope of the curve at the origin.³⁹ These considerations are implicit in the curve presented as Fig. 1.

III. METHOD OF CALCULATION

A. Outline

The procedure we follow for calculating f values is to first compute 1S and 1P wave functions variationally, and then use these wave functions to compute oscillator strengths as described earlier. The method of calculation of 1S wave functions for the Be isoelectronic sequence has been given previously,¹³ and for the Be 1S ground state we use in this work the first 105 terms of the 107-term wave function reported in that work. The 1S wave functions for CIII and OV, the other two members of the Be isoelectronic sequence computed in this work, are 89-configuration truncations of the 107-term wave function with different orbital exponents; these will be presented later in this paper.

The 1P wave functions used in this work differ from the 1S wave functions in that they are derived from configurations containing three S -type STO's and one P -type STO in order to obtain an over-all P symmetry. The O_{as} projection treatment of spin, final Hamiltonian, and overlap matrix elements is similar to the treatment in Ref. 13, but the $O(L^2)$ projection is different.

B. $O(L^2)$ Projection

For the $O(L^2)$ projection we use the formula of Löwdin⁴⁰:

$$O_{L, M_L}^{L^2} = (2L+1) \frac{(L+M_L)!}{(L-M_L)!} \times \sum_{\nu=0}^{L_{\max}-L} (-1)^\nu \frac{L_-^{L-M_L+\nu} L_+^{L-M_L+\nu}}{\nu!(2L+\nu+1)!}, \quad (36)$$

where L_+ and L_- are the (step-up and step-down) operators $L_+ = L_x + iL_y$, $L_- = L_x - iL_y$. For $L = M_L = 0$, Eq. (36) reduces to

$$O_{1,0}^{L^2} = 3 \sum_{\nu=0}^{L_{\max}-L} (-1)^\nu \frac{L^{\nu+1} L^{\nu+1}}{\nu!(\nu+3)!}. \quad (37)$$

TABLE I. Orbital exponents chosen for the wave functions of this work.

	State Be I		C III		O V	
	1S	1P	1S	1P	1S	1P
ns^a	3.6847 ^b	3.6903	5.6575	5.6734	7.6295	7.6564
ns''	0.9562 ^b	1.0851	1.8316	1.7685	2.6903	2.6152
np	6.2 ^c	...	9.7 ^c	...	13.2 ^c	...
np''	1.1 ^c	0.4897 ($2p''$) 0.5600 ($3p''$)	2.5 ^c	1.946 ^c	3.9 ^c	2.998

^a Unless otherwise noted, values are taken from Ref. 44.

^b Reference 43.

^c Reference 41.

TABLE II. 53-configuration wave function for the 1P states of Be I, C III, and O V.

Config. No. n	Configuration	Coefficient of 53-term wave function		
		Be I	C III	O V
1	$1s^2 2s'' 2p''$	4.764 777	4.456 084	4.030 196
2	$1s^2 2s'' 2p'' r_{12}$	$9.858 159 \times 10^{-2}$	$7.125 036 \times 10^{-2}$	$6.164 211 \times 10^{-2}$
3	$1s^2 2s'' 2p'' r_{12}^2$	$1.301 724 \times 10^{-1}$	$9.009 462 \times 10^{-2}$	$6.036 654 \times 10^{-2}$
4	$1s 2s 2s'' 2p''$	$7.136 297 \times 10^{-1}$	$2.062 765 \times 10^{-1}$	$1.520 908 \times 10^{-1}$
5	$1s 3s 2s'' 2p''$	$4.777 081 \times 10^{-1}$	$-1.096 418 \times 10^{-1}$	$-5.247 793 \times 10^{-2}$
6	$2s^2 2s'' 2p''$	$-3.610 930 \times 10^{-1}$	$-7.524 009 \times 10^{-2}$	$-6.204 963 \times 10^{-2}$
7	$1s^2 3s'' 3p''$	-2.236 168	$-1.254 405 \times 10^{-1}$	$-6.857 813 \times 10^{-2}$
8	$1s^2 3s'' 2p''$	$-1.547 299 \times 10$	-7.897 644	-5.826 508
9	$1s^2 2s'' 2p'' r_{34}^2$	1.338 971	$4.474 569 \times 10^{-1}$	$3.809 192 \times 10^{-1}$
10	$1s^2 3s'' 2p'' r_{34}^2$	$-1.340 863 \times 10$	-3.445 850	-2.645 772
11	$1s^2 3s'' 2p'' r_{12}$	$1.356 403 \times 10^{-1}$	$-2.627 807 \times 10^{-2}$	$-2.208 844 \times 10^{-2}$
12	$1s^2 3s'' 2p'' r_{12}^2$	$-1.698 274 \times 10^{-1}$	$-9.194 345 \times 10^{-2}$	$-6.797 355 \times 10^{-2}$
13	$1s 2s 2s'' 3p''$	$-7.270 678 \times 10^{-1}$	$-1.001 716 \times 10^{-1}$	$-9.503 281 \times 10^{-2}$
14	$2s^2 2s'' 3p''$	$3.076 321 \times 10^{-1}$	$2.335 176 \times 10^{-2}$	$2.420 712 \times 10^{-2}$
15	$1s 2s 3s'' 2p''$	-1.254 746	$-4.610 471 \times 10^{-1}$	$-3.643 951 \times 10^{-1}$
16	$1s^2 2s'' 2p'' r_{34}$	-3.009 266	$-7.613 410 \times 10^{-1}$	$-5.540 680 \times 10^{-1}$
17	$1s^2 3s'' 2p'' r_{34}$	2.606 178 $\times 10$	7.453 266	5.174 738
18	$1s 4s 2s'' 2p''$	$2.734 655 \times 10^{-1}$	$2.896 810 \times 10^{-1}$	$2.242 952 \times 10^{-1}$
19	$1s^2 1s'' 2p''$	$-6.549 024 \times 10^{-1}$	$-9.442 578 \times 10^{-1}$	$-9.468 604 \times 10^{-1}$
20	$1s^2 4s'' 2p''$	$2.725 431 \times 10$	9.304 938	6.063 070
21	$1s^2 3s'' 3p'' r_{12}$	$-1.400 753 \times 10^{-1}$	$9.903 329 \times 10^{-3}$	$6.318 000 \times 10^{-3}$
22	$1s 2s 3s'' 3p''$	$5.625 126 \times 10^{-1}$	$1.336 102 \times 10^{-2}$	$1.178 410 \times 10^{-1}$
23	$1s 3s 3s'' 3p''$	$2.336 654 \times 10^{-1}$	$-3.549 046 \times 10^{-2}$	$-2.944 542 \times 10^{-2}$
24	$1s 3s 3s'' 2p''$	$-2.688 191 \times 10^{-1}$	$8.032 144 \times 10^{-2}$	$4.233 014 \times 10^{-2}$
25	$2s^2 3s'' 3p''$	$-2.609 941 \times 10^{-1}$	$-2.122 250 \times 10^{-2}$	$-2.245 426 \times 10^{-2}$
26	$2s^2 3s'' 2p''$	$2.401 137 \times 10^{-1}$	$2.114 013 \times 10^{-2}$	$2.389 507 \times 10^{-2}$
27	$1s^2 4s'' 2p'' r_{34}$	-4.511 435 $\times 10$	-1.467 124 $\times 10$	-9.644 455
28	$1s^2 4s'' 2p'' r_{34}^2$	2.469 396 $\times 10$	7.941 418	5.594 460
29	$1s 2s 2s'' 2p'' r_{12}$	$5.713 677 \times 10^{-1}$	$5.249 247 \times 10^{-1}$	$3.994 919 \times 10^{-1}$
30	$1s 2s 2s'' 2p'' r_{12}^2$	$-3.613 879 \times 10^{-2}$	$-6.697 089 \times 10^{-3}$	$7.209 994 \times 10^{-3}$
31	$1s 3s 2s'' 2p'' r_{12}$	$-8.156 346 \times 10^{-1}$	$-8.029 208 \times 10^{-1}$	$-6.131 649 \times 10^{-1}$
32	$1s 3s 2s'' 2p'' r_{12}^2$	$4.765 640 \times 10^{-1}$	$4.269 118 \times 10^{-1}$	$3.125 237 \times 10^{-1}$
33	$2s^2 2s'' 2p'' r_{12}^2$	$-2.554 983 \times 10^{-2}$	$-2.725 063 \times 10^{-2}$	$-2.186 619 \times 10^{-2}$
34	$1s 4s 2s'' 2p'' r_{12}^2$	$-1.588 584 \times 10^{-1}$	$-1.378 832 \times 10^{-2}$	$-1.003 420 \times 10^{-1}$
35	$1s^2 5s'' 2p''$	-2.103 935 $\times 10$	-5.652 667	-3.353 813
36	$1s^2 5s'' 2p'' r_{34}$	3.626 329 $\times 10$	1.196 395 $\times 10$	7.502 105
37	$1s^2 5s'' 2p'' r_{34}^2$	-1.994 613 $\times 10$	-7.432 937	-4.957 139
38	$1s^2 6s'' 2p''$	7.150 092	1.454 424	$7.532 903 \times 10^{-1}$
39	$1s^2 6s'' 2p'' r_{34}$	-1.268 021 $\times 10$	-3.235 979	-2.194 769
40	$1s^2 6s'' 2p'' r_{34}^2$	6.969 993	2.588 735	1.640 764
41	$1s 2s 2s'' 2p'' r_{34}$	$-8.271 090 \times 10^{-1}$	$-2.441 955 \times 10^{-1}$	$-1.862 829 \times 10^{-1}$
42	$1s 2s 2s'' 2p'' r_{34}^2$	$7.409 538 \times 10^{-1}$	$5.009 553 \times 10^{-2}$	$4.410 859 \times 10^{-2}$
43	$1s 3s 2s'' 2p'' r_{34}$	$-8.067 233 \times 10^{-1}$	$-1.628 441 \times 10^{-2}$	$-1.016 370 \times 10^{-2}$
44	$1s 3s 2s'' 2p'' r_{34}^2$	$1.981 111 \times 10^{-1}$	$1.100 518 \times 10^{-2}$	$-9.469 788 \times 10^{-4}$
45	$1s^2 4s'' 2p'' r_{12}$	$1.044 517 \times 10^{-2}$	$-1.572 072 \times 10^{-5}$	$-5.212 241 \times 10^{-3}$
46	$1s^2 4s'' 2p'' r_{12}^2$	$-1.382 374 \times 10^{-1}$	$-1.031 250 \times 10^{-1}$	$-7.445 267 \times 10^{-2}$
47	$1s^2 3s'' 3p'' r_{12}^2$	$3.872 209 \times 10^{-2}$	$-2.453 043 \times 10^{-3}$	$-1.296 422 \times 10^{-3}$
48	$1s 2s 3s'' 2p'' r_{34}^2$	1.699 981	$5.061 419 \times 10^{-1}$	$3.692 899 \times 10^{-1}$
49	$1s 2s 3s'' 2p'' r_{34}^3$	-1.194 784	$-2.307 126 \times 10^{-1}$	$-1.842 234 \times 10^{-1}$
50	$1s 3s 3s'' 2p'' r_{34}^2$	$1.871 062 \times 10^{-1}$	$1.606 919 \times 10^{-2}$	$1.873 209 \times 10^{-2}$
51	$1s 2s 4s'' 2p''$	$-2.428 041 \times 10^{-2}$	$-7.975 607 \times 10^{-2}$	$-5.431 176 \times 10^{-2}$
52	$1s 3s 4s'' 2p''$	$1.017 389 \times 10^{-1}$	$9.991 232 \times 10^{-2}$	$6.226 619 \times 10^{-2}$
53	$2s^2 4s'' 2p''$	$-1.686 599 \times 10^{-2}$	$-1.303 484 \times 10^{-2}$	$-1.057 253 \times 10^{-2}$

For the configurations we use (three *S*-type STO's and one *P*-type STO), $L_{\max} = 1$ and Eq. (37) becomes simply

$$O_{1,0}^{L^2} = (3/3!)L_-L_+; \quad O_{1,0}^{L^2}Y_{10} = \frac{1}{2}\sqrt{2}Y_{10}. \quad (38)$$

C. Integral Treatment

To complete the evaluation of all matrix elements needed for this work, a scheme is needed to handle the two-, three-, and four-electron integrals of the form

$$\int f_1(\vec{r}_1)f_2(\vec{r}_2)f_3(\vec{r}_3)f_4(\vec{r}_4) \times g_1(r_{12})g_2(r_{23}) \cdots g_k(r_{34})dv. \quad (39)$$

The treatment of these integrals has been described in detail in a previous publication.³⁴

IV. CHOICE OF PARAMETERS AND CONFIGURATIONS

The wave functions employed here for the 1S and 1P states of Be I, C III, and O V are of the form [Eq. (1)]

$$\psi = \sum_k C_k \Phi_k, \quad (40)$$

where Φ_k is a properly antisymmetrized and projected product of χ , STO's defined by Eq. (2), and an $r_{ij}^{\nu_k}$ factor. The STO basis is, in the Weiss⁴¹

notation, the basis set $1s, 2s, \dots, ns, 2p, \dots, np$ for the inner shell; $1s'', 2s'', \dots, ns'', 2p'', \dots, np''$ for the outer shell. The STO orbital exponents [ζ in Eq. (4)] used in this work are given in Table I with references to the works from which they were taken. No attempt was made to optimize the exponents, since it was felt that costly insignificant improvements would have been made to the energies obtained.¹³ However, Weinhold's scheme for computing upper and lower bounds does have the feature that the orbital exponents can be varied directly with respect to *S* and its bounds, so that experimentation with shorter-length wave functions may be justified.⁴²

The 105-configuration and 89-configuration 1S wave functions used in this work were truncations of the 107-term wave function reported in Ref. 34, with exponents as listed in Table I.^{41, 43, 44} The 53-configuration 1P wave functions used in this work are given in Table II, where under configuration is listed only the unique

$$r_{ij}^{\nu_k} \prod_{s=1}^4 \Phi_{ks}(\vec{r}_s)$$

part of Φ_k as defined by Eq. (2).

V. RESULTS

The results of the calculations we have done are presented in Table III, where we tabulate $|\tilde{W}_0|$,

TABLE III. Computed values for Be I, C III, and O V (in amu).

Configs.		$ \tilde{W}_0 $	\mathcal{S}	$^1S \rightarrow ^1P$ transition		$E(^1P)$	ΔE_{calc}	E_{nonrel}	
1S	1P			f	$E(^1S)$			1S	1P
Be I									
46 × 18	0.930 01	10.869	1.405 87	-14.661 55	-14.443 17	0.218 38	-14.666 2	-14.472 67	
89 × 53	0.909 73	10.400	1.344 7	-14.666 485	-14.472 457	0.194 03			
105 × 53	0.909 34	10.391	1.343 6	-14.666 546	-14.472 457	0.194 09			
C III									
89 × 53	0.442 61	2.1494	0.765 37	-36.533 37	-36.062 83	0.470 54	-36.534 03	-36.067 67	
O V									
89 × 53	0.291 37	1.0668	0.514 62	-68.409 57	-67.684 33	0.725 24	-68.412 11	-67.688 56	
Configs.		$\langle \psi_b (3/4\pi)X_0X_0 \psi_b \rangle$	S_{a-}	S_{b-}	Δ_{ab}	$W_{<}$	$W_{>}$	$f_{<}$	$f_{>}$
1S	1P								
Be I									
46 × 18	5.126 75	0.989 77	0.795 42	2.064 42	0.497 94	1.224 52	0.402 8	2.431 3	
89 × 53	4.517 69	0.999 75 ^a	0.998 62	1.920 95	0.865 49	0.952 61	1.217 1	1.477 58	
105 × 53	4.517 69	0.999 86 ^a	0.998 62	1.921 14	0.876 36	0.940 98	1.247 9	1.438 69	
C III									
89 × 53	0.717 64	0.999 75 ^a	0.996 65 ^a	0.722 31	0.425 07	0.458 61	0.705 91	0.821 73	
O V									
89 × 53	0.298 96	0.999 53 ^a	0.999 01 ^a	0.462 67	0.276 75	0.305 59	0.464 25	0.556 06	

^a These values were computed using Weinberger's formula, Ref. 45.

the absolute multiplet strength S , the f values, term energies, the relative term energy $\Delta E = E(^1P) - E(^1S)$, and various quantities related to the calculation of upper and lower bounds to f . In evaluating S_{a-} and S_{b-} , either Eq. (24) was used or Weinberger's formula⁴⁵

$$S^2 \geq \frac{E_{n+1} - J_0}{E_{n+1} - E_0} \prod_{\nu=1}^n \frac{E_{\nu} - J_0}{E_{\nu} - E_0} \frac{J_{\nu} - E_0}{J_{\nu} - J_0}, \quad (41)$$

where E_0, E_1, \dots, E_{n+1} are the $n+2$ lowest eigenvalues of H and the J_i are the corresponding Rayleigh-Ritz estimates $\langle \phi_i | H | \phi_i \rangle$. Here the ϕ_i are approximations to the exact eigenfunctions and it is assumed that

$$E_0 \leq J_0 \leq E_1 \leq J_1 \leq \dots \leq E_n \leq J_n \leq E_{n+1}. \quad (42)$$

To use either Eq. (24) or (41), one must know either the nonrelativistic energies E_n or their lower bounds. For Be, the 107-term energy of Ref. 13 was obtained after examining 145 terms; the maximum energy contribution of the 38 terms which were dropped at various stages of the calculation was 0.000 072 amu. This gives us an "exact" nonrelativistic energy estimate of -14.666 62 amu for the Be ground state. To obtain the nonrelativistic energy estimate for the other states, we add the experimentally determined relative term energies to the ground-state estimate. The nonrelativistic energy estimates for CIII and OV states were obtained in the same manner, with the 1S ground-state nonrelativistic energy estimates being taken from Weiss.⁴¹

For BeI, calculations were done on (i) the 46-term 1S wave function obtained by dropping all terms from the 105-term 1S wave function with $E_n - E_{n-1} < 0.001$ amu and the 18-term 1P wave function obtained from the first 18 terms of the 53-term 1P wave function; (ii) the 89-term 1S wave function obtained by dropping all terms from the 105-term 1S wave function with $E_n - E_{n-1} < 0.001$ amu and the 53-term 1P wave function; and (iii) the 105-term 1S wave function and the 53-term 1P wave function. For calculations (i) and (ii), the term in brackets in Eq. (23) is small,⁴⁶ so that, approximately,

$$W_{ab} \approx S_{a\pm} S_{b\pm} \bar{W}_{ab} \pm \epsilon_{a+} S_{b\pm} \Delta_{ab}. \quad (43)$$

Since in going from the 89-configuration 1S wave function to the 105-configuration 1S wave function, $|W_0|, f$, and Δ_{ab} change by $< 0.2\%$, it would appear that going to even more accurate 1S wave functions would merely tighten the theoretical upper and lower bounds, without changing the f value (to $\leq 2\%$). Therefore, we feel that the computed f values are probably within 1% of the true values. Arguments may be advanced in support of this

TABLE IV. $\Delta E = E(^1P) - E(^1S)$ for Be I, C III, and O V (in amu).

	ΔE	
	Calc.	Obs.
Be I	0.194 09	0.193 95
C III	0.470 54	0.466 36
O V	0.725 24	0.723 55

conclusion.

(a) Extremely good wave functions on an energy criterion were employed for both the 1S and 1P states. The 53-term 1P wave function gave an energy of -14.472 57 amu, as compared with our exact nonrelativistic energy estimate of -14.472 67 amu. This estimate involves an assumption that relativistic effects are the same for 1S and 1P states. Tatewaki *et al.*⁴⁴ argue that the relativistic correction for a $2p$ electron in the L shell rather than a $2s$ electron is < 0.0001 amu for Be. However, Verhaegen and Moser⁴⁷ place the relativistic correction at < 0.001 amu, so that the 1P wave function may not be as accurate as claimed. In any event, for calculations (ii) and (iii) the accuracy of the 1P wave function is not critical, since in Eq. (43) it is only ϵ_{a+} and not ϵ_{b+} which is critical for accurate bounds.

(b) We obtain extremely good values for the difference in term energies $\Delta E = E(^1P) - E(^1S)$. This could be fortuitous, i.e., the energy difference is more accurate than either $E(^1S)$ or $E(^1P)$. The calculated and experimental energy differences are tabulated in Table IV for BeI, CIII, and OV.

Taking 2% accuracy as a guide, we notice that at every step of the calculation the bounds do not reflect the true accuracy of the calculation. The bounds calculations are particularly bad in the 46×18 case, which leads to the conjecture that the bounds formulas require trial wave functions which closely approximate the exact wave function

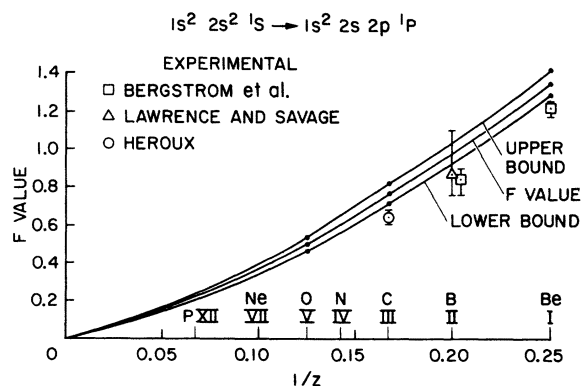


FIG. 1. F value as a function of $1/Z$ for various elements.

TABLE V. Recent theoretical calculations of oscillator strengths.

		Be I		C III		O V	
		HF	CI	HF	CI	HF	CI
Burke <i>et al.</i> ^a	length l	1.774	1.4237	1.0746	0.7930	0.7055	0.5250
	velocity v	1.0132	1.3862	0.5627	0.8047	0.3039	0.4922
Weiss ^b	l	1.813	1.410	1.112	0.770	0.741	0.517
	v	0.951	1.455	0.537	0.843	0.353	0.570
This work	l		1.3436		0.765 37		0.514 62
		NIV					
Nussbaumer ^c	l	0.64					

^a Reference 53.^c Reference 33.^b A. W. Weiss (private communication).

or else the bounds may be substantially different from the exact result and thus not very useful.⁴⁸ However, it should be pointed out that no attempt has been made to optimize the basis orbital exponents with respect to S and its bounds.

For CIII and OV we have employed 89-configuration wave functions, since the BeI calculation showed that the f value doesn't change much in going to a 105-term expansion. The rigorous bounds obtained are on the same level of accuracy as the BeI case, in which (i) there are more interleaving J 's [Eq. (42)] to employ in the Weinberger estimates [Eq. (41)] and (ii) Δ_{ab} is much smaller.

In Fig. 1⁴⁹⁻⁵¹ we graph our results as discussed earlier. The results for BeI, CIII, and OV are extrapolated to $Z^{-1}=0$ using the Z -expansion results of Weiss as a guide.³⁹ A few experimental results are included for comparison. The experimental results are uniformly too low and in most cases the error estimates appear unrealistic. Wiese⁵² has conjectured that the experimental failure is due to cascading effects in the beam-foil experiments.

A few recent theoretical calculations, which include configuration interaction (CI), have been done. The f values of these calculations are shown in Table V along with our best values. These previous calculations treat the $1s^2$ core as being fixed, and yield results which appear to be too high. In addition, the agreement of length and velocity is seen not to be an accurate measure of the error in the calculations. (Burke *et al.*⁵³ report a calculation for BeI in which length and velocity results give 1.3863 and 1.3860, respectively, although they recommend the values in Table V.) Thus, neglect of core (and intershell) correlation in this case (lowest $^1S-^1P$ transition for the Be

isoelectronic sequence) appears to give results in error by approximately 5-10%, at least for BeI.

VI. CONCLUSIONS

On the basis of the results presented here,⁵⁴ it seems reasonable to conclude that the introduction of r_{ij} coordinates for an atomic wave function with $N > 3$ can lead to reliable f values (~2% accuracy). It also appears that to obtain reliable upper and lower bounds to oscillator strengths, wave functions of considerable accuracy must be employed. A level of accuracy for less-exact calculations which neglect core correlations has been established for the Be isoelectronic sequence. In addition, recommended values for the entire Be-isoelectronic-sequence $1s^2 2s^2 ^1S-1s^2 2s 2p ^1P$ transition have been presented (Fig. 1).

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Note added in manuscript. Figure 1 depicts the experimental status as of 1971. The experimental status as of 1973 is depicted in Fig. 2 of Ref. 55. The basic picture doesn't change; all the beam-foil measurements seem to be consistently low. The experiment that seems to be in the best shape is that of Lawrence and Savage, Ref. 50, which is a phase-shift measurement. We thank Dr. A. W. Weiss for bringing this reference to our attention.

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